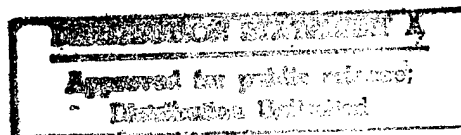


OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 98PR00368-00
Contract/Grant Number: N0001493310058
Contract/Grant Title: Surface Chemistry of Non-Fouling Coating Polymeric Materials
Principal Investigator: Joseph A. Gardella, Jr., Professor of Chemistry, SUNY Buffalo
Mailing Address: Department of Chemistry, State University of New York at
Buffalo, Buffalo, NY 14260-3000
Phone Number: 716-645-6800 X2111 FAX Number: 716-645-5994
E-mail Address: gardella@acsu.buffalo.edu http address: www.acsu.buffalo.edu/~gardella

- a. Number of papers submitted to refereed journals, but not published: 7
b. + Number of papers published in refereed journals (for each, provide a complete citation): 3
c. + Number of books or chapters submitted, but not yet published: 0
d. + Number of books or chapters published (for each, provide a complete citation): 1
e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
f. Number of patents filed: 0
g. + Number of patents granted (for each, provide a complete citation): 0
h. + Number of invited presentations (for each, provide a complete citation): 3
i. + Number of submitted presentations (for each, provide a complete citation): 9
j. + Honors/Awards/Prizes for contract/grant employees (list attached): 7
(This might include Scientific Society Awards, Offices, Selection as Editors, Promotions, Faculty Awards/Offices. etc.)
k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:
Graduate Students: 4
Post-Doctoral Associates: 1 (0.5 time supplemented by Korea Science Fdn. Award) including the number of,
Female Graduate Students: 2 (each serving about 50% time on the ONR Award)
Female Post-Doctoral Associates: 0
Minority* Graduate Students: 1 (full time with supplemental minority fellowship)
Minority* Post-Doctoral Associates: 0
Asian Graduate Students: 3 (each serving about 50% time on the ONR Award)
Asian Post-Doctoral Associates: 1
1. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)
+ Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published.

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OFFICE OF NAVAL RESEARCH
END-OF-THE-YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT N00014-93-3-10058

PR Number 98PR00368-00

Surface Chemistry of Non-Fouling Coating Polymeric Materials

Professor Joseph A. Gardella, Jr., P. I.

Department of Chemistry
State University of New York at Buffalo
Buffalo, NY 14260-3000

August 17, 1998

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a. Papers Submitted to Refereed Journals

J. Chen, H.-Z. Zhuang, J. Zhao and J. A. Gardella, Jr. "Solvent Effects on Polymer Surface Structure", *Critical Reviews in Surface Chemistry*, submitted, July, 1998

J. X. Chen and J. A. Gardella, Jr. "Solvent Effects on Surface Composition of Poly(dimethylsiloxane)-co-polystyrene/Polystyrene Blends", *Macromolecules*, submitted April, 1998.

J. Zhao, S. R. Rojstaczer, M. Z. Xu and J. A. Gardella, Jr. "Effect of Siloxane Segment Length on the Surface Composition of Polyimidesiloxane Copolymers and its Role in Adhesion", *Macromolecules*, submitted March 1998.

J. Zhao, M. H. Na, T. D. Wood, J. A. Gardella, Jr. and H. Luo, "ToF-SIMS Depth Profiling of Multiple Quantum Well II-VI Semiconductors Using Negative Cluster Ions", *Journal of Vacuum Science and Technology*, submitted January, 1998.

J. Zhao, S. R. Rojstaczer and J. A. Gardella, Jr. "Surface Composition and Morphology of Polyimidesiloxane Copolymers with Short Polydimethyl siloxane Segments Studied by ESCA and ToF-SIMS", *J. Vac. Sci. Technol.*, accepted, in press

J. Zhao, M. H. Na, E. H. Lee, H. C. Chang, J. A. Gardella, Jr. and H. Luo, "The Surface Chemistry of II-VI Semiconductors Studied by ToF-SIMS and XPS", *J. Vacuum Science and Technology*, Part B: submitted January, 1998, reviewed, resubmitted, July, 1998

E. J. Bekos, F. O. Fally, L. Sun, D. E. Carney, M. Konaklieva, P. J. McKeown and J. A. Gardella, Jr. "Covalent Binding of a Peptide by its N-Terminus to a Hydroxylated Fluoropolymer Surface", *Langmuir*, submitted August, 1996, revised, resubmitted August, 1998.

b. Papers Published in Refereed Journals

J. Chen and J. A. Gardella, Jr., "Quantitative ATR-FTIR Analysis of Surface Segregation of Polymer Blends of Polystyrene/Poly(dimethyl siloxane)-co-polystyrene" *Applied Spectroscopy*, **1998**, 52, 361-6.

J. Zhao, M. H. Na, T. D. Wood, J. A. Gardella, Jr. and H. Luo, "Mass Distributions of Negative Cluster Ions of II-VI Semiconductors Detected by Time of Flight Secondary Ion MS", in *Secondary Ion Mass Spectrometry XI*, G. Gillen, R. Lareau, J. Bennett and F. Stevie, Eds., John Wiley and Sons, **1998**, 969-72.

J. Zhao, S. Rojstaczer and J. A. Gardella, Jr., "Determination of Segment Length Distribution of Polyimidesiloxane Copolymers with Short Polydimethyl siloxane Segments", in *Secondary Ion Mass Spectrometry XI*, G. Gillen, R. Lareau, J. Bennett and F. Stevie, Eds., John Wiley and Sons, **1998**, 521-4.

c. Books or chapters Submitted

none

d. Books or Chapters Published

F. Fally, E. J. Bekos, T. S. Koloski, D. M. Ammon, Jr. and J. A. Gardella, Jr., "Covalent Binding of the C- or N- Termini of Peptides to a Hydroxylated Fluoropolymer Surface by Applying Different Coupling Chemistries", Proceedings of the International Conference on Polymer Solid Interfaces: From Model to Real Systems, J. J. Pireaux, J. Delhalle and P. Rudolph, Eds, 1998, Presses Universitaires de Namur (Namur, 1998).

e. Printed Technical Reports/non-refereed papers

none

f. Patents Filed:

none

g. Patents Granted:

none

h. Invited Presentations by the PI.

"Polymer Surface Chemistry: How Characterization Drives Synthesis and Structure Property Development", Abstracts of the 44th Annual Meeting of the American Vacuum Society (AVS), San Jose, CA, October 20-24, 1997.

"Surface Chemistry of Materials in the Environment: Detection, Design and Fundamental Mechanisms of Biological Interactions" Environmental Engineering and Sciences Seminar, Department of Civil, Structural and Environmental Engineering, SUNY Buffalo, November 7, 1997.

"Polymer Surface Chemistry in Biological and Environmental Applications", Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, December 4, 1997.

i. Submitted Presentations

W.-Y. Yan and J. A. Gardella, Jr. "Monolayer Surface Chemistry of PEO Langmuir Blodgett Films: Studies by Time of Flight SIMS", 1997 Gordon Conference on Organic Thin Films, Salve Regina, RI, July 21-25, 1997.

J.-X. Chen and J. A. Gardella, Jr. "Potential Coatings Based on Block Copolymer/Homopolymer Blends: Studies of Surface Composition of PDMS-co-PS/PS Blends", 1997 Gordon Conference on Coatings and Films, New Hampshire, July 21-25, 1997.

W.-Y. Yan and J. A. Gardella, Jr. "Time of Flight Secondary Ion Mass Spectrometry Study of Ion Formation Mechanisms: Effects of End Group Chemistry", Abstracts of the Eleventh International

Conference on Secondary Ion Mass Spectrometry (SIMS XI), Orlando, FL, September 7-12, 1997.

A. M. Hawkrigde, J. A. Gardella, Jr. and A. J. Pertsin, "Time of Flight Secondary Ion Mass Spectrometry Studies of Monodisperse Cycloliner Poly(dimethyl siloxane)" Abstracts of the Eleventh International Conference on Secondary Ion Mass Spectrometry (SIMS XI), Orlando, FL, September 7-12, 1997.

J. Zhao, S. Rojstaczer and J. A. Gardella, Jr., "Determination of Segment Length Distribution of Polyimidesiloxane Copolymers with Short Polydimethyl siloxane Segments", Abstracts of the Eleventh International Conference on Secondary Ion Mass Spectrometry (SIMS XI), Orlando, FL, September 7-12, 1997.

J. Zhao, M. H. Na, T. D. Wood, J. A. Gardella, Jr. and H. Luo, "Mass Distributions of Negative Cluster Ions of II-VI Semiconductors Detected by Time of Flight Secondary Ion MS", Abstracts of the Eleventh International Conference on Secondary Ion Mass Spectrometry (SIMS XI), Orlando, FL, September 7-12, 1997.

J. X. Chen, N. L. Hernandez-de Gatica, and J. A. Gardella, Jr., "Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) Study of Hydrolysis of Poly (glycolic acid)", Abstracts of the Eleventh International Conference on Secondary Ion Mass Spectrometry (SIMS XI), Orlando, FL, September 7-12, 1997.

R. W. Nowak, J. A. Gardella, Jr., T. D. Wood, P. A. Zimmerman and D. M. Hercules, "Ion Formation Mechanisms of Tertiary Structures of Polymers in Time of Flight Secondary Ion Mass Spectrometry", Abstracts of the Eleventh International Conference on Secondary Ion Mass Spectrometry (SIMS XI), Orlando, FL, September 7-12, 1997.

J. Zhao, S. R. Rojstaczer and J. A. Gardella, Jr. "Surface Composition and Morphology of Polyimidesiloxane Copolymers with Short Polydimethyl siloxane Segments Studied by ESCA and ToF-SIMS", Abstracts of the 44th National Symposium of the American Vacuum Society, San Jose, CA, October 20-24, 1997.

j. Honors/Awards/Prizes for Contract/Grant Employees
J. A. Gardella, Jr.

Editorial Boards

CRC Critical Reviews in Surface Chemistry, Colloids and Surfaces: Part B: Biointerfaces,
Spectroscopy Letters

Honors

Distinguished Alumni Award (2nd), 1998, Oakland University Department of Chemistry

Scientific Society Offices

Treasurer, WNY ACS Analytical Group/SAS Niagara Frontier Section (1990-98)

University Committee Chair/Administrative Positions

SUNY Buffalo Environmental Task Force, Chair (Appointed by President William Greiner, November, 1995).

Director, Materials Research Instrumentation Facility (MRIF), part of the Center for Advanced Photonic and Electronic Materials, SUNY Buffalo, August, 1996.

M. A. Patterson

Increased Representation in Science (IRIS) Fellowship Award, sponsored by Coca-Cola Foundation

Jin Zhao

Student Award for the Best Paper at the Applied Surface Science Division, American Vacuum Society 44th National Meeting

I. Other Funding

- 1.) Title: Polymer Surface Chemistry: Structure and Reactivity of Surface Segments and Oligomeric Chain Distributions
Agency: National Science Foundation, Chemistry Division, Anal. Surf. Chem.
Amount: 295,000
Duration: 8/1/97-5/30/00
Relationship to ONR Funding: This project supports three graduate students studying the fundamentals of surface analysis by ESCA, FTIR, SIMS, etc., for polymer and organic thin films. Special emphasis on low surface energy polymers, multicomponent polymers, surface rearrangements and surface reactivities of biodegradable polymers. Some overlap to ONR in more fundamental issues of quantitation of polymer surface structure and reactivity. Focused on polymer reactivity and biodegradation more specifically than ONR program.
- 2.) Title: Support for Daniel Ammon and Wen Yan Yan, Ph.D. students
Agency: Bausch and Lomb, Inc.
Amount: unspecified
Duration: unspecified
Relationship to ONR Funding: This project supports two graduate student jointly studying protein adsorption on hydrogel materials and polyethylene oxide surface and bulk structure. The development of a low temperature probe for vitreous samples is directly related to performing "wet, frozen" analysis under the ONR program. Wen Yan Yan's work has direct scientific relationship with the ONR grant. Part of matching funding for Item 6 Below.
- 3.) Title: Adhesive Microspheres For Treating Bowel Diseases
Agency: Brown University Subcontract; National Institutes of Health
Total Award: \$25,000
Duration: 48 Months (5/1/94-4/30/98)
Person Months/Year Committed to Project: 2% CY
Co-PI's: PI: at Brown University, Professor Edith Mathiowitz, ABC Section, Division of Biology and Medicine
Relationship to ONR Funding: None. This program provides support for instrumental analysis by ESCA of biodegradable polymers synthesized by Professor Mathiowitz' group at Brown.
- 4.) Title: Fundamental Studies of Plasma Surface Modification Into Porous Fluoropolymeric Membrane Materials: Optimization and Surface Chemical Analysis
Agency: Integument Technologies, Inc.
Total Award: \$16,500
Period: 12 Months (7/1/97 - 12/31/98)
Person Months/Year Committed to Project: none
Relationship to ONR Funding: None. This program funds the development of plasma modification techniques for biomaterials and membranes based on fluoropolymers.

- 5.) Title: High Surface Area Fluoropolymeric Support Materials for Biotechnological Applications (Year II)
Agency: Center for Biotechnology, New York State Center for Advanced Technology, SUNY Stonybrook
Total Award: \$25,000
Period: 12 Months (7/1/97 - 6/30/98)
Person Months/Year Committed to Project: 5% Calendar Year
Relationship to ONR Funding: None. This program provides support for the adaptation of plasma modification techniques for fluoropolymers to powders and other high surface area polymers.
- 6.) Title: Contact Lens Process Analysis by Multiple Methods of Mass Spectrometry
Agency: Center for Biotechnology, New York State Center for Advanced Technology, SUNY Stonybrook
Total Award: \$24,954
Period: 13 Months (6/1/98 - 6/30/99)
Person Months/Year Committed to Project: 5% Calendar Year
Co-PI: T. D. Wood, Department of Chemistry, SUNY Buffalo
Relationship to ONR Funding: Some Overlap This program provides support for the development of quantitative SIMS, MALDI and ESI-FTMS as applied to process analysis for hydrogel polymer mixtures used for soft contact lens formulations. Overlaps with ONR program in that students working on low temperature sample handling procedures for water immersion of polymers under ONR program will also utilize this approach in this research program for SIMS work.
- 7.) Title: Improved Access to Environmental Analysis for Community Groups
Agency: Environment and Society Institute, SUNY Buffalo, Environmental Management Alternatives Program (EMAP)
Total Award: \$17,000
Period: 12 Months (8/1/98 - 7/30/99)
Person Months/Year Committed to Project: 5% Calendar Year
Relationship to ONR Funding: None. This project develops public service learning for chemistry, geology, geography, biology and civil engineering students as applied to community based research projects joint with City of Buffalo, local industry and community groups.

PROPOSALS SUBMITTED FOR EXTERNAL REVIEW:

Pending Research Support J. A. Gardella, Jr. (PI):

- 1.) Title: Surface Chemistry of Non-Fouling Coating Polymeric Materials
Agency: Office of Naval Research, Chemistry Division, MIMI Program.
Amount: 295,000
Duration: 10/1/98-9/30/01
Relationship to ONR Funding: Renewal of present grant.

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PART II

for

GRANT N0001493310058

PR Number 98PR00368-00

Surface Chemistry of Non-Fouling Coating Polymeric Materials

- a. Principal Investigator: Professor Joseph A. Gardella, Jr., P. I.
- b. Current Telephone Number:
716-645-6800 X2111 Office, 716-645-6963 or 716-645-5994 FAX
- c. Cognizant ONR Scientific Officer: Dr. Kenneth Wynne
- d. Program Objectives

Three program goals are pursued which are related to the surface chemistry of potential non-fouling coatings. 1. New analytical methods will be developed for determining fundamental surface structure property relationships, especially for critical microstructural and bonding details in the topmost surface region. Special emphasis is placed on methodologies for the study of samples exposed to simulated marine environment. 2. Coordinated surface analytical determinations of the effects of structure, processing and treatment are applied to a variety of multicomponent (especially block, blend and graft co-) polymers. We are cooperating with a number of ONR funded polymer chemists, who are synthesizing new materials with potentially interesting surface properties (e.g. T. Chapman, A. Malik). New model surfaces with multiple chemical environments need to be synthesized for challenge to questions about the effects of surface and bulk structure on surface properties, specifically bioadhesion or bioabhesion. 3. The study of controlled conformations of model biopolymers on polymeric surfaces by SIMS and HREELS will complete the examination of the fundamentals of the initial stages of biopolymer film formation.

e. Significant Results

In the past year, seven projects have been underway under this grant.

1. We completed an extensive study of the surface structure and adhesion of siloxane polyimide (SIM) copolymers (see research highlight). This study showed that short siloxane segments ($n=1-9$) copolymerized with imide functionalities create an adhesive polymer with a dominant surface excess of siloxane controlled not by the bulk composition of siloxane, but by the segment lengths. Short segment lengths of siloxane yielded low surface excess of siloxane and shallow siloxane surface excess regions. This yielded the highest peel strengths for the adhesive. We hypothesized that the adhesion was related to how close the polyimide segments were placed to the air surface, that upon melt pressing the adhesive to metal surfaces that rearrangement of the polyimide regions yielded a metal polyimide interfacial bonding region responsible for the strong adhesion. Further, tests of the pure polyimide yielded a lower peel strength, indicating the need for the soft siloxane to allow reorganization and mediate towards strong adhesion to metals. The implication for MIMI studies is that a short siloxane length places hard segments close to surfaces and allows rearrangements under high surface energy conditions. Thus, instead of seeking to add large amounts of siloxane to polymer surfaces to create low energy minimal fouling surfaces, polymers and mixtures should be formulated to allow long siloxane chains to orient near the surface pushing hard segments as far away from the surface as possible.
2. We have applied Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) determinations of surface molecular weight distributions to a series of segmented siloxane polymers. We are synthesizing specialized model systems of narrow molecular weight PDMS segmented polymers including polyurethane (with long PDMS segments) and polyimides (with short PDMS segments).
3. We have used quantitative angle dependent and low temperature, environmental ESCA and FTIR-ATR to analyze a series of siloxane block copolymer-homopolymer blends as processed by various solvent mixtures and exposed to water to examine rearrangement of the polymer surface upon simulated marine exposure. One paper on the quantitative analysis with FTIR-ATR was published and one other paper on the combined results of solvent optimization has been submitted.
4. We have completed two studies of reactive metal interfaces with polymers, extending the study of a polyether urethane on 316L stainless steel. At present, the latter work involves the study of the simulated seawater corrosion (free and accelerated) of the stainless steel surface and the study of simulated microbial biocorrosion by acetic acid exposure and delamination of coating without degradation.
5. We have continued our collaboration with Professor Pireaux's group in Belgium in the quantitative understanding of HREELS vibrational spectroscopy of polymer surfaces. A paper was submitted and two others are in preparation.

6. We have used ToF-SIMS to study the end group chemistry and conformation of polyethylene oxides, a known minimal protein adsorber.
7. We continued our collaboration with Professor Toby Chapman at Pittsburgh on the surface chemistry of polyethylene oxide and polypropylene oxide graft macromonomer-copolymers using ESCA and ToF-SIMS. We have begun work with Dr. Aslam Malik on the surface structure of polyfluorooxetane polymers (polyFOX).

f. Plans for next year's work

1. Synthesize a series of new siloxane polymers with urethane and imide hard segments. Study the distribution of segments at the surface using ToF-SIMS and quantitative angle dependent ESCA. Copolymerize mixtures of segment lengths to create model systems for study of the competition between short and long segment lengths in formulating a surface excess of siloxane at the surface.
2. Continue characterization of multicomponent block copolymers and blends and the study of solvent casting effects as a means to promote a controlled surface composition. In particular work on defined siloxane block/segment length polymers synthesized through polyimide and polyurethane technology with narrow (single) molecular weight polydimethyl siloxane prepolymers.
3. Study the surface structure and composition of urethane and SIM copolymers after simulated marine exposure using low temperature sample handling devices on SIMS and ESCA.
4. Extend collaborative surface analysis to other MIMI Polymer Science investigators and provide substrata for further biological adhesion measurements.

g. List of names of graduate students and postdoctoral fellows currently working on this project.

Dr. Won Ki Lee, Ph.D., Pusan University, Korea, Postdoctoral Fellow, ½ funding from Korea Science Foundation

Dr. Ilario Losito, Ph.D., University of Bari, Italy, Postdoctoral Fellow

Marc Patterson, Graduate Student (*minority graduate student, Ph.D. completed August, 1997, current appointment as NAS-NRC Postdoctoral with Dr. Irwin Singer of NRL on the surface chemistry of corrosion protection of steels by polymers*)

Jiaxing Chen, Graduate Student

John Strong, Graduate Student

Wen Yan Yan, Graduate Student (female)

Jin Zhao, Graduate Student

Adam Hawkrige, Graduate Student

Christine Mahoney, Graduate Student (female)